

Re-examining the electronic structure of germanium: A first-principle study

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We report results from an efficient, robust, ab-initio method for self-consistent calculations of electronic and structural properties of Ge. Our non-relativistic calculations employed a generalized gradient approximation (GGA) potential and the linear combination of atomic orbitals (LCAO) formalism. The distinctive feature of our computations stem from the use of Bagayoko-Zhao-Williams-Ekuma-Franklin (BZW-EF) method. Our results are in agreement with experimental ones where the latter are available. In particular, our theoretical, indirect band gap of 0.65 eV, at the experimental lattice constant of 5.66 Å, is in excellent agreement with experiment. Our predicted, equilibrium lattice constant is 5.63 Å, with a corresponding indirect band gap of 0.65 eV and a bulk modulus of 80 GPa. We also calculated the effective masses in various directions with respect to the Γ point.

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There has been great interest in germanium (Ge) due to the central role it plays in modern electronics. As a consequence of this interest, there has been many experimental [1–13] as well as theoretical [12, 14–19] studies, with the latter utilizing computational techniques of varying sophistications, ranging from tight binding method, the empirical pseudopotential method, and density functional theory (DFT) methods to approaches that entirely go beyond DFT.

Generally, DFT [20–24] is the most widely used ab initio theory in modern computational studies of electronic properties of materials. Angle resolved photoemission and X-ray resonant emission spectra [1, 2] show that the upper valence bands for traditional *sp* semiconductors and metals are well reproduced within the local density functional approximation (LDA) to DFT. However, the low-lying conduction bands are severely underestimated, leading to the well-known band gap problem.

The Green function, G , and the screened Coulomb interaction, W , method (GW) has been used to accurately reproduce the band gap and other properties of Ge. However, the GW results do not lead to any significant changes in the dispersion of the upper valence bands [25] as compared to DFT findings, but rather a rigid shift in their energies and a reduction of the calculated valence-band width [15]. In most GW methods, the Dyson equation is not solved self-consistently [16], resulting in a violation of charge conservation [26]. From the work of Ku and Eguiluz [16], it is evident (as pointed out by the authors) that even though their calculated band gap is in agreement with experiment, low-lying empty states near the X point are severely underestimated.

Heyd-Scuseria-Ernzerhof (HSE) hybrid functional [27, 28] calculations reported an indirect gap in the range 0.63 – 0.77 eV [29–31]. The latter authors [29–31] did not publish any electronic energies at the high symmetry points of Ge. The HSE approach involves a range separation

of the exchange energy into some fractions of nonlocal Hartree-Fock exchange and of DFT exchange potentials. There are several versions of HSE [27, 28, 30, 32, 33]. The approach generally entails a range separation parameter, ω , which varies between 0 and ∞ . There exists a value of ω that gives the correct gap for a given system; this value is adjusted from one system to another [30, 31, 34].

The theoretical underestimations of band gaps and other energy eigenvalues have been ascribed to the inadequacies of DFT potentials for the description of the ground state electronic properties of Ge [15, 16, 19]. Other methods [15, 16, 19, 25, 30, 35] that entirely go beyond DFT do not obtain the band gap value of Ge and related electronic structure quantities without adjustments or fitting parameters. Further, to the best of our knowledge, there is no rigorous theoretical results predicting (or addressing) the indirect band gap of Ge. This unsatisfactory situation is a key motivation for our work. A concomitant motivation is to attain a highly accurate, ab-initio, self-consistent computational capability that lends itself to informing and guiding the design and fabrication of semiconductor based devices.

The possibility for the referenced attainment has been stated by Bagayoko and co-workers [36–38], despite perceived limitations of DFT in the literature. They explained the fact that the derivative discontinuity of the exchange correlation energy has yet to be proven to be non-zero in semiconductors [36], even though some believe it to be non-zero. Perdew *et al.* [39], following a thought experiment on a diatomic molecule, established the existence of a derivative discontinuity of the exchange correlation energy. Generalizing this derivative discontinuity to the case of semiconductors, Perdew and Levy [40] showed that the exchange correlation potential may jump by the discontinuity, Δ_{xc} , when the number of electrons in the system under study increases by one. In their work on this discontinuity in insulators, Sham

and Schlüter [41] explicitly stated that while they established the existence of the discontinuity, they could not determine whether it is zero or not in real insulators. Subsequent work by Sham and Schlüter [42] derived the discontinuity of the functional derivative of E_{xc} in insulators by considering an increase of the number of electrons by one. Cautiously, these authors concluded that the discrepancy between calculated and measured band gap is a measure of the discontinuity Δ_{xc} - given the results from several calculations - if the employed LDA potentials are assumed to be good approximations. The description of our method below indicates the strong possibility that some current LDA and GGA potentials may be very good approximations. Computational approaches may be sources of the discrepancy, as the perceived limitations of DFT, described in the literature, are far from being settled. This statement is supported in part by several DFT results, including predictions, in excellent agreement with experiment [36, 43]. An ampler discussion of the derivative discontinuity and of effects of computational approaches is provided in the supplementary material.

Ge has an experimental, indirect band gap ($E_g^{\Gamma-L}$) of 0.664 eV at room temperature [44]. Theoretical calculations using several techniques have led to band gaps of Ge in the ranges of -0.02 to 0.35 eV for LDA and GGA [15, 45] and of 0.51 to 0.94 eV for the GW method [15, 16]. In most of these GW results, the position of the conduction band minimum (CB_{min}) is not at the L point. For instance, in the work of Ku and Eguluz [16], it is at the X point for their $\sum_{GW}[G_{GW}]$, $\sum_{GW}[G_{LDA}]$, and $\sum_{GW}[G_{LDA}] + \text{no } 3d's$ methods since their predicted band gap $E_g^{\Gamma-X}$ value of 0.71, 0.49, and 0.49 eV are smaller than the corresponding 0.79, 0.51, 0.51 eV for $E_g^{\Gamma-L}$. However, their PS-based + CPP method obtained correctly the position of CB_{min} . A similar trend can be seen in the work of Fleszar [15] where $E_g^{\Gamma-\Gamma}$ of 0.57 eV is smaller than $E_g^{\Gamma-L}$ of 0.62 eV, and in cases where the ordering is correct, the gap is over-estimated by ~ 0.3 eV. The work of Aulbur et al. [19] found the lowest eigenvalue energies at the high symmetry points to be ~ 1.0 eV over-estimated. The same can be said of several other GW results [25, 35] where the gap of Ge is found to be direct instead of indirect, as established by experiment.

In this letter, we present a simple, robust approach based on basis set optimization [37, 38, 43]. We use this method to calculate the electronic and structural properties of Ge and compare our results to experiments.

In the ground state, Ge crystallizes in the diamond structure (space group: $O_h^7 - Fd\bar{3}m$) [46–48] with room temperature lattice constant of 5.66 Å [47].

Our ab initio, self consistent, nonrelativistic calculations employed a linear combination of atomic orbitals (LCAO). We utilize the electronic structure package from the Ames Laboratory of the US Department of Energy (DOE), Ames, Iowa [49]. For the LDA computations,

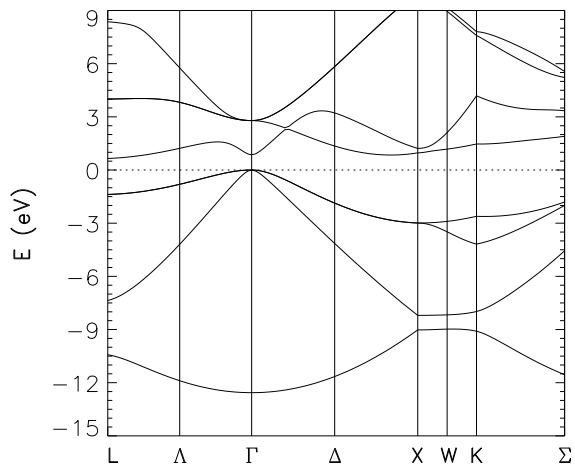


FIG. 1: Calculated band structure of Ge, as obtained using our GGA BZW-EF optimal basis set. The horizontal, dotted line denotes the position of the Fermi energy (E_F) which has been set equal to zero. The calculated indirect band gap ($E_g^{\Gamma-L}$) of 0.65 eV is basically the same as the room temperature experiment one of 0.66 eV [44].

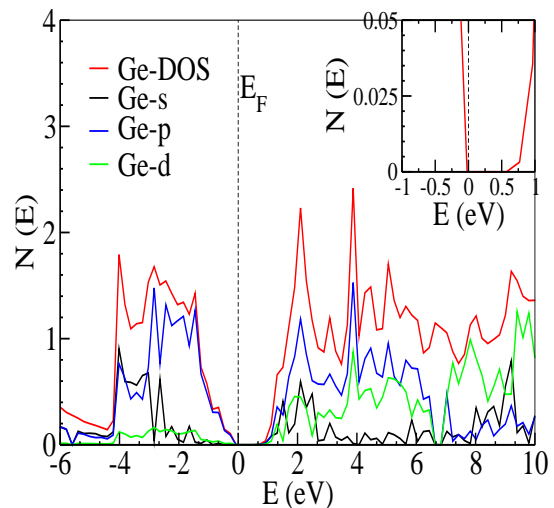


FIG. 2: (Color online). Calculated density of states (DOS) and partial DOS of Ge, as obtained using our GGA BZW-EF optimal basis set. The vertical, straight, dashed line denotes the Fermi energy (E_F) which has been set equal to zero. As per the insert, it clearly shows the energy band gap.

we used the Ceperley and Alder density functional approximation (DFT) exchange-correlation functional [50] as parameterized by Vosko-Wilk-Nusair [51]. We refer to it as the CA-VWN LDA potential. The GGA calculations were carried out using the Ceperley and Alder DFT exchange correlation contribution [50] as parameterized by Perdew and Wang [52–54]. We refer to it as the CA-PW GGA potential.

The distinctive feature of our calculations is the use of the Bagayoko, Zhao, Williams, Ekuma, and Franklin

(BZW-EF) method [38, 55]. In the BZW method, [37, 38, 43, 55–59] a minimum of three successive, self-consistent calculations are performed. For the first one, a relatively small basis set, no smaller than the minimum basis set that accounts for all the electrons in the system, is employed. This set is augmented with one orbital for the second calculation. Depending on the s , p , d , or f nature of this orbital, 2, 6, 10, and 14 functions, respectively, are added to the basis set. The occupied energies of Calculation I and II are compared graphically and numerically. They are generally different, with eigenvalues from Calculation II being lower or equal to corresponding ones from I. This process of adding one orbital and of performing self-consistent calculations is continued until a calculation is found, say N , to have the same occupied energies as Calculation $(N+1)$ that immediately follows it. Then, the outputs of Calculation N provide the LDA/GGA BZW description of the material under study. The basis set for this calculation is the optimal basis set, i.e., the smallest one that leads to the minima of all the occupied energies. In Calculation $(N+1)$ and others with larger basis sets that include the optimal basis set, the charge density, the potential, and the Hamiltonian do not change as compared to their values from Calculation N ; nor do the occupied energies. These calculations, however, do lead to the lowering of some unoccupied energies on account of the basis set and variational effect stemming from the Rayleigh theorem [38, 60]. For Ge, the basis set of Calculation III was the optimal one [Ge ($3s3p3d4s4p4d5p$), for the valence states only], where the $4d$ and $5p$ orbitals are unoccupied.

The enhancement of the original BZW method is in the methodical increase of the basis set in our calculations. This enhancement leads to adding p , d , and f polarization orbitals, for a given principal quantum number, before adding the spherically symmetric s orbital. These additional unoccupied orbitals are needed to accommodate the reorganization of the electron cloud, including possible polarization, in the crystal environment. For valence electrons in molecules to solids, polarization has primacy over spherical symmetry. The BZW method has been shown to lead to accurate ground state properties of many semiconductors: c-InN [59], w-InN [58], w-CdS [37], c-CdS [61], rutile-TiO₂ [43], SrTiO₃ [38] AlAs [62], GaN, Si, C, RuO₂ [56], and carbon nanotubes [63]. Details of our method have been explicitly explained in the literatures [37, 38, 43, 55, 56, 60, 61].

The Brillouin zone (BZ) integration for the charge density in the self consistent procedure is based on 28 special k points in the irreducible Brillouin zone (IBZ). The computational error for the valence charge is 2.3×10^{-5} eV per valence electron. The self consistent potential converged to a difference of 10^{-5} after several tenths of iterations. The energy eigenvalues and eigenfunctions are then obtained at 161 special k points in the IBZ for the band structure. A total of 89 weighted k points, cho-

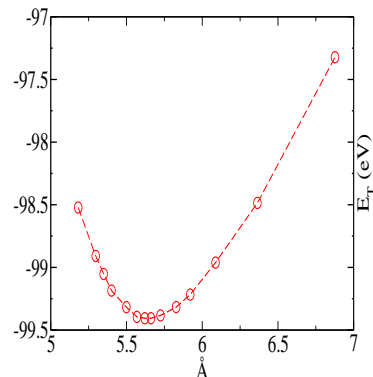


FIG. 3: (Color online). Calculated total energy per unit cell (E_T) as a function of the lattice constant (\AA) of Ge, as obtained with the GGA BZW-EF optimal basis set. The calculated equilibrium lattice constant is 5.63 \AA , is little smaller than the room experimental value of 5.66 \AA , as expected.

sen along the high symmetry lines in the IBZ of Ge, are used to solve for the energy eigenvalues from which the electron density of states (DOS) are calculated using the linear analytical tetrahedron method [66]. The partial density of states (pDOS) and the effective charge at each atomic sites are evaluated using the Mulliken charge analysis procedure [67]. We also calculated the equilibrium lattice constant a_o , the bulk modulus (B_o), the associated total energy, and the electron and hole effective masses in different directions.

In calculating the lattice constant, we utilized a least square fit of our data to the Murnaghan's equation of state [68]. The lattice constant for the minimum total energy is the equilibrium one. The bulk modulus (B_o) is calculated at the equilibrium lattice constant.

The difference in energy between the GGA BZW-EF and LDA BZW-EF computational results is small ~ 0.05 eV. Thus, the results reported here are those from GGA BZW-EF unless otherwise stated. The results of the electronic structure are given in Figs. 1 and 2. Total energy versus lattice constant data are as shown in Fig. 3 while Table I shows the eigenvalue energies at various high symmetry points in the Brillouin zone.

Our ab-initio, first principle results show that the fundamental gap of Ge is an indirect one with the maximum of the valence band (VB_{max}) occurring at Γ and the minimum of the conduction band (CB_{min}) at the L point (cf. Figs. 1 and 2 and Table I). Our calculated indirect gap, using the equilibrium lattice constant, is 0.649 eV, while the indirect band gap value using the experimental lattice constant is 0.652 eV. Our calculated direct gap at the Γ point is 0.857 eV (cf. Table I). Our calculated indirect band gap value using the LDA BZW-EF is 0.644 eV with a corresponding direct gap of 0.857 eV. The LDA and GGA potentials lead to the same direct gap, while the LDA indirect gap is 8 meV smaller than that for GGA. Our calculated values are in good agreement with experimental room temperature indirect band gap value of 0.664 eV and direct band gap value in the range 0.805 – 0.895 eV [44, 69]. The accurate, calculated values for the indirect and direct gaps of Ge are a significant improvement over some previous results that employed methods

TABLE I: The calculated electronic energies (eV) of different bands at high symmetry points in the Brillouin zone of Ge, as obtained by GGA BZW-EF calculations, compared to experimental ones where the latter are available. Experimental data are from Refs. [3, 5, 47, 64, 65].

GGA BZW-EF			EXP		GGA BZW-EF			EXP		GGA BZW-EF			EXP	
Γ	-12.56	-12.6 \pm 0.3	K	-9.09	-10.10 \pm 0.2	X	-9.02	-9.3 \pm 0.2	L	-10.42	-10.60 \pm 0.50			
	0.00	0.00		-7.98	N/A		-8.20	-8.65		-7.36	-7.70 \pm 0.20			
	0.86	0.90		-4.18	-4.20 \pm 0.20		-3.00	-3.15 \pm 0.20		-1.38	-1.40 \pm 0.30			
	2.79	3.01		-2.61	N/A		0.97	N/A		0.65	0.70, 0.76			
				1.47	N/A		1.22	1.16		4.00	4.20			
				4.19	N/A		9.84	N/A		8.36	7.90			
				7.59	N/A									
				7.81	N/A									
W	-8.98	N/A	Σ	-11.55	N/A	Δ	-11.65	N/A	Λ	-11.89	N/A			
	-8.17	N/A		-4.56	-4.30 \pm 0.20		-4.14	N/A		-4.19	N/A			
	-3.49	N/A		-2.00	N/A		-1.87	N/A		-0.81	N/A			
	-2.90	N/A		-1.80	N/A		1.35	N/A		1.22	N/A			
	1.18	N/A		1.90	N/A		3.22	N/A		3.82	N/A			
	2.11	N/A		3.34	N/A		5.84	N/A		5.76	N/A			
	8.95	N/A		5.21	N/A									
	9.15	N/A		5.56	N/A									

(or approaches) beyond DFT [15, 16, 19, 25, 35]. Our calculated spectra shown in Fig. 2, especially for the valence states, are in good agreement with experiments [3, 4, 6–8, 70]. The same can be said of our calculated bands, as shown in Fig. 1, which are in good agreement with experiment [5, 71]. The occupied bandwidth is calculated to be 12.56 eV, in very good agreement with room temperature values of 12.6 ± 0.3 [3, 5, 47, 64].

From Fig. 2, in the DOS of valence states, we predict two weak shoulders at -0.31 and -0.67 eV, and a peak at -1.50 eV. This peak is followed by relatively broad ones at -1.90, -2.41, and -2.86 eV, before two sharp peaks at -4.06 and -7.41 eV. In the conduction bands, a small shoulder can be found at 0.71 eV followed by a peak at 2.10 eV. Other peaks can be seen at 3.07, 3.88, 4.44, and 5.06 eV. The position of these critical points are in good agreement with experiments [3–9, 13, 64, 65, 72, 73]. For instance, scanning tunneling spectroscopy measurements of Feenstra [9] reported peaks in the valence states at -0.47 ± 0.06 eV and -1.23 ± 0.030 eV while the inverse photoemission spectra of Jackson et al. [73] reported peaks at 2.40 ± 0.10 , 4.20 ± 0.10 , and 5.50 ± 0.10 eV. We note that our spectra are not broadened as it is the case in (many) experiments; they may therefore have more features.

From Fig. 2, significant contributions of $3d$ states can be seen in both the valence and conduction bands. Even though Ge is known to be an sp material, the correct treatment of $3d$ states and others as valence ones is critical for accurate results. Crystal symmetry gives rise to polarizations that are absent in isolated atom. In our work, only Ge ($1s2s2p$) were considered to be in the core.

The importance of this view has been highlighted by the work of Shirley et al. [74] and confirmed by those of Ku and Eguluz [16] and of Rohlfling et al. [25]. It generally leads to a better description of the band structure energies, especially in obtaining the fundamental, indirect gap of Ge.

Effective masses are measures of the accuracy of a method as they depend very sensitively on the curvatures of the bands. They determine in part the transport properties, the Seebeck coefficient, and the electrical conductivity of materials. The calculated electron effective masses at the bottom of the conduction band along the Γ - L , Γ - X , and Γ - K directions, are 0.043 - 0.051, 0.043 - 0.051, and 0.043 - 0.052 (all in units of the electron mass), respectively. These results are in good agreement with experiment [47].

The total energy versus the lattice constant data are shown in Fig. 3. The data fit well to the Murnaghan equation of state (EOS) [68]. The calculated bulk modulus, B_o , is 80 GPa, in close agreement with experimental values of 75 – 80 GPa [44, 75, 76]. We also calculated the equilibrium lattice constant from the total energy minimization. The calculated equilibrium lattice constant is 5.63 Å. The experimentally reported room temperature lattice constants are in the range of 5.62 to 5.66 Å [44, 46].

In summary, our results show that the electronic and related properties of Ge can be accurately described, with LDA/GGA potentials, by a careful search for a basis set that is verified to be complete for the description of the ground states.

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SUPPLEMENTARY MATERIAL

Despite the great progress made possible by density functional theory (DFT), from 1964 to present, problems associated with obtaining theoretically the measured energy or band gaps, for finite and crystalline semiconductors, respectively, have persisted. Specifically, most DFT calculations, with emphasis on those utilizing local density approximation (LDA) and semi-local potentials, have led to semiconductor band gaps that are 30 – 50% smaller than their corresponding, measured values. Much effort has been deployed to find explanations of and remedies to this recalcitrant band gap problem. Perdew and Zunger [77] introduced the self interaction correction (SIC) to local spin density (LSD) approximation calculations. While the exact functional for the ground state is self interaction free, these authors discussed corrections that appear to be needed for the description of finite systems, beginning with atoms, and of localized states in solids. This self interaction is argued to contribute to the underestimation of the band gaps of insulators by DFT calculations [77]. Consequently, self interaction corrections (SIC) are expected to improve the agreement between calculated band gaps and measured ones, in addition to improving binding energies and bringing orbital energies closer to removal energies [77, 78]. While self interaction corrections have led to some improvements in band gap calculations, they have not totally resolved the problem. Applications of SIC have mostly overestimated the band gap of semiconductors [79, 80]. According to Cohen *et al.* [81], self interaction is well-defined only for one-electron systems.

According to the literature, a major source of the theoretical underestimation of band gaps consists of the derivative discontinuity of the exchange correlation energy, Exc [39–42]. Perdew *et al.* [39], following a thought experiment on a diatomic molecule, established the existence of a derivative discontinuity of the exchange correlation energy, i.e., a discontinuity in the exchange correlation potential, V_{xc} . Perdew and Levy [40] generalized this discontinuity to the case of semiconductors. They showed that the exchange correlation potential may jump by the discontinuity, Δ_{xc} , when the number of electrons in the system under study increases by one. Band gaps calculated with a local density

approximation (LDA) potentials, according to their findings, are to be augmented by this discontinuity in order to reproduce the corresponding, measured values. The authors suggested, without claiming to have a proof of it, that this discontinuity is a non zero (and positive) in real semiconductors and insulators. Sham and Schlüter [41] also found a derivative discontinuity of E_{xc} in semiconductors. These authors, however, asserted that their work does not show whether or not this discontinuity is non zero in real insulators. Subsequent work by Sham and Schlüter [42] derived the discontinuity of the functional derivative of E_{xc} in insulators by considering an increase of the number of electrons by one. Cautiously, these authors concluded that the discrepancy between calculated and measured band gap is a measure of the discontinuity Δ_{xc} - given the results from several calculations - if the employed LDA potentials are assumed to be good approximations. The description of our method below indicates the strong possibility that some current LDA and GGA potentials may be very good approximations.

Despite its popular use to explain the disagreement between calculated and measured band gaps, the above discontinuity has not yet been established to be non zero in real semiconductors or insulators. Further, Sham and Schlüter [42] underscored the fact that, in principle, DFT and Kohn Sham LDA hold only if the number of particle is kept constant. The question could arise whether or not the discontinuity, derived by considering a change of the number of particle, is strictly applicable to DFT or LDA calculations. From the preceding, it has not yet been established that DFT or LDA calculations cannot obtain the correct band gaps, despite the fact that presently known LDA potentials do not have a discontinuity and that most of the numerous, previous ab-initio DFT and LDA calculations did not.

Another presumed contributor to the band gap underestimation by theory stems from the use of local (LDA) and semi-local (GGA) potentials. The question naturally arises as to what extent the local and semi-local potentials fail to capture key feature of the exact one. We are aware of no definitive answer, given that the exact one is not known. We would have had to delve into this matter further if we were dealing with molecules or their dissociation. The solid state systems of interest to us, to judge by previous results obtained with our method [36, 59], possible errors due to the use of local and semi-local potentials appear to be very small.

There exist several approaches that have been introduced to address the band gap problem. Review articles and books are the best sources for discussing these approaches and for examples of the many DFT calculations that led to band gaps much smaller than their corresponding, experimental counterparts. In contrast, a summary of results from BZW LDA calculations for over 10 materials show agreement between theory and experiment. Illustrative examples of discrepancies between theory and experiment follow. The case of Ge is summarized in this article. Some previous LDA, GGA, and GW calculations did not yield the measured band gap, from first principle. A table provided by Ekuma and Bagayoko [43] shows a multitude of DFT calculations with vastly different band gaps for titanium dioxide. With the computational method described here, Ekuma and Bagayoko obtained the measured, direct gap and predicted an indirect one. For elemental silicon, Grüning *et al.* [82] reported an LDA band gap of 0.7 eV, much smaller than the 1.25 eV they reported as the measured value. These authors also performed calculations with the exact exchange (EXX), EXX plus LDA, EXX plus the random phase approximation (RPA). The last approach or scheme yielded 0.6 eV, a gap smaller than the above LDA gap, while the first two led to 1.5 and 1.6 eV respectively, values much larger than the experimental one. With the original version of our method, Zhao *et al.* utilized an LDA potential to obtain a gap of 1.02 for Si, much closer to the experimental one. Generalized gradient approximation (GGA) calculations have led to improvements of calculated properties of materials, including lattice parameters. Specifically, Hao *et al.* [83] reported revised Tao-Perdew-Staroverov-Scuseria (revTPSS) meta-GGA calculated lattice parameters that are in agreement with experiment following a zero-point phonon correction, for over 50 materials. Despite this very significant success, most GGA and meta-GGA calculations, including the previous ones discussed here for Ge, have not produced band gaps in agreement with experiment.

From the above summary, historical overview of the band gap problem, it appears that the scientific community believes that the derivative discontinuity of the exchange correlation energy is the main source of the disagreement between DFT calculated energy and band gaps and their corresponding, measured ones. This belief led to the development of several schemes aimed at resolving the band gap problem. Except for the few, most of these schemes are ad hoc as they include adjustable parameters that vary with the material under study. The continuing growth in the number of these schemes seems to be a problem in itself, the ad hoc nature of most of them does not lend itself to predictive capabilities from first principle, the aim of theory to inform and to guide experiment. The only exception of the above trend consists of the work of our group. This work has not yet gotten the attention of the community at large, presumably due to the strength of the above belief, on the one hand, and the preponderance of results that are explained with the discontinuity. As we previously noted [58], the situation resembles that of the Ptolemaic model of the solar system where epicycles were continually introduced to explain its disagreement with observations. The quintessential point in support of our method, described below, is the following: For all DFT calculations of energy bands, the *minima of the occupied energies, which add up to yield the ground state energy of the electron system, are obtained from the theory if the “correct” ground state charge density is utilized, subject to the constraint*

that the number of particle is kept constant [20, 21].

Most of the previous DFT calculations, including those with GGA and LDA potentials, have consisted of judicious selecting large basis set and of performing iterations to obtain self consistent eigenvalues of the Kohn-Sham type equation. It is assumed that the single basis set in question leads to the correct representation of the electronic cloud in the system under study, a system that can be drastically different from an atomic or ionic one. *In particular, as we recently pointed out, polarization (p , d , and f orbitals) has primacy over spherical symmetry (s orbital) for systems varying from diatomic molecules to solids.* Hence, utilizing basis sets derived from calculations of properties of atoms for the study of solids is potentially problematic. Indeed, the angular symmetries in these systems are vastly different from those for atoms and ions. The need for the method described below becomes apparent with the realization that, irrespective of the degree of convergence of the iterations, a single trial basis set that has a major symmetry inadequacy for the description is not going to lead to physically valid DFT eigenvalues as the implacable condition of using the “correct” ground state density will not be met.

The original version of our method, named after Bagayoko, Zhao, and Williams (BZW) was introduced in 1998 [60] and further explained in 1999 [56]. The method consists of implementing the linear combination of atomic orbitals (LCAO) formalism by methodically searching for the smallest basis set, called the optimal basis set, that leads to the minima of the occupied energies. This search begins with a deliberately small basis set that is not smaller than the minimum basis set, i.e., the smallest one needed to account for all the electrons in the system. The self consistent calculation with this basis set is followed by another whose basis set uses the previous one plus one additional orbital. The occupied energies from the two calculations are compared numerically and graphically. In the more than 20 systems we have studied, these occupied energies from these first two calculations have been different, with those of calculation II generally lower than the corresponding one from Calculation I. Calculation III is then carried out, using the basis set in Calculation II plus an additional orbital. The occupied, self consistent energies from Calculations II and III are also compared. This process of augmenting a basis set, performing a new calculations, and comparing its results with those of the one immediately preceding it, continues until a calculation is found, say N, to have exactly the same occupied energies as the one immediately following it. This perfect superposition establishes that the minima of the occupied energies have been reached and that the corresponding basis set give the best representation of the ground state charge density of the system.

Before elaborating further on the physical content of the method, we note that adding an orbital means increasing the size of the basis set (and hence the dimension of the Hamiltonian) by 2, 6, 10, or 14 depending on the s , p , d , or f character, respectively, of the orbital in question. In the original BZW, we added orbitals in the order of their energies resulting from the atomic calculations, i.e., the orbitals corresponding to the lowest laying excited, atomic state were successively added. As apparent from our earlier results, the BZW method practically led to the measured band gap of semiconductors we studied. Further, our predictions of the band gaps and other properties for cubic Si_3N_4 [84] and cubic InN [59] were totally confirmed by experiment [85–87]. Following the works of Ekuma and Franklin [37, 38, 43, 61], we realized that valence electrons in multi-atomic systems simply do not follow the symmetry landscape that prevail for isolated atoms or ions. The aim is to obtain a better representation of the electronic cloud (ground state charge density) of the system under study. Hence, in most of our subsequent calculations, for a given principal quantum number, we add p , d , and f (if applicable) orbitals before the s orbital for that principal quantum number. This counter-intuitive ordering, for isolated atoms, is simply needed for ‘some’ multi-atomic systems. The initials of Ekuma and Franklin (EF) are added to the name of the enhanced method [BZW-EF] in recognition of their extensive calculations whose results led Bagayoko to see the necessity for this new order. While the BZW method led to band gaps that were sometimes smaller by 0.1 – 0.3 eV, insignificant differences between BZW-EF calculated gaps and corresponding experiment ones are in the second decimal place for the systems studied to date. The BZW-EF method led to an upper valence band width more than 1.0 eV larger than was obtained with the BZW, with a significant improvement in agreement with experiment.

The origin of the changes in the band structure and the band gap when the basis set increases toward the optimal one consists of the progressively better representation of the ground state charge density. As per the derivation of DFT, the minima of the occupied energies are obtained if “correct” charge density for the ground state is employed. These changes are due to physical interactions, given that the charge density, the potential and hence the Hamiltonian change from one calculation to the next. We should underscore here that while our focus is on occupied energies (i.e., DFT is a fundamentally ground state theory), when these energies reach their minima, so do the low laying unoccupied energies, up to 9 – 10 eV for the materials studied to date with the BZW-EF method. For the many systems with the BZW, most low laying unoccupied energies also converged up to 5 – 6 eV, as was the case for wurtzite indium nitride [88]. For a few materials, this convergence of the lowest unoccupied energies was not achieved with the original BZW method. As shown by Zhao *et al.* [56] the low-laying unoccupied energies converge when the occupied ones do, due to the fact that at least one band crosses the Fermi level. This fact may partly explain the early successes of DFT in

describing metals as compared to semiconductors.

The description of what occurs when basis sets much larger than the optimal ones are employed will complete the description of the BZW-EF method. We first recall that the basis set immediately following the optimal one leads to the occupied energies obtained with the optimal one and to the same unoccupied energies up to 9 – 10 eV. So, by much larger basis sets, we mean the ones that are larger than the basis sets immediately following the optimal ones. Earlier works by Zhao and Co-workers [56, 60] verified that basis sets larger than the optimal one do not change the charge density, the potential, and the Hamiltonian, nor do they change the occupied energies. In the absence of changes in the Hamiltonian, i.e., the physics of the study, the additional lowering of unoccupied energies with these much larger basis set cannot be ascribed to DFT. However, the Rayleigh theorem provides an explanation of the unphysical lowering of these energies. The theorem states that when the same eigenvalue equation is solved with two basis sets of different size, such that the larger one includes the smaller one, then the eigenvalue obtained with the larger basis set are lower or equal to their corresponding one obtained with the smaller basis set.

Clearly, after the optimal basis set is reached, and that the occupied energies are no longer changed from their values obtained with the optimal one, the lowering of unoccupied energies can be ascribed to a mathematical artifact that is the manifestation of the above theorem. We therefore contend that this extra lowering, a variational basis set effect [56, 60], is a major source of discrepancies between many previous DFT calculations and between these calculations and experiment, as far as band gaps are concerned. *The lowest laying conduction bands, with full physical meaning when they result from the optimal basis set, partly lose their physical content due to the above effect.* It is important to note that this is the case for any basis set that is not the optimal one, whether it is smaller or larger than the optimal, or simply lacks orbital or angular features of the optimal one. For basis sets that do not totally include their corresponding optimal ones, even the occupied energies are not totally DFT results. The preceding lines in this paragraph point to the great difficulty in obtaining physically meaning DFT occupied and low laying unoccupied energies with a single trial basis set, irrespective of the degree of convergence of the applicable iterations for self consistency.
